

Magnetic states at the Oxygen surfaces of ZnO and Co-doped ZnO

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(Dated: April 25, 2008)

First principles calculations of the O surfaces of Co-ZnO show that substitutional Co ions develop large magnetic moments which long-range coupling depends on their mutual distance. The local spin polarization induced at the O atoms is three times larger at the surface than in the bulk, and the surface stability is considerably reinforced by Co. Moreover, a robust ferromagnetic state is predicted at the Oxygen (0001) surface even in the absence of magnetic atoms. The occurrence of surface magnetic moments correlates with the number of p -holes in the valence band of the oxide, and the distribution of the magnetic charge is, even in the absence of spin-orbit interaction, highly anisotropic.

Keywords: dilute magnetic oxides, p -magnetism, ZnO, Co

The prediction of room-temperature (RT) ferromagnetism (FM) in dilute magnetic oxides generated a large interest, and at present there is wide experimental evidence for insulators such as ZnO, TiO₂ and SnO₂ when doped with just a few percent of magnetic transition-metal (TM) ions [1]. One of the most promising and extensively studied systems is Co-ZnO [2]. However, its magnetic properties and in particular RT-FM remain controversial, since they are not only strongly dependent on the preparation method, but also on the growth conditions of the samples [3]. The initial agreement between experimental observation of FM and calculations has evolved to the questioning of the possibility of RT-FM either mediated by valence-band holes, or due to the percolation of magnetic polarons [4, 5]. Moreover, controversial issues need to be explained: the independence of the Curie temperature (T_C) on the concentration of Co, that magnetic moment (mm) per cation may exceed the limiting value established by Hund's rules or the time decay of the magnetization [6]. Nevertheless FM, though dependent on the growth conditions, has been reported in low-dimensional ZnO structures, even when undoped or doped with non-magnetic elements [7].

Despite ferromagnetic (F) order is mainly observed in low-dimensional structures with multiple surfaces and interfaces, to our knowledge there is not a theoretical study exploring how the surface affects the magnetic state of dilute oxides. In this Letter we investigate the local magnetic order at the polar (0001) oriented surfaces of wurtzite ZnO. We show that Oxygens at Co-ZnO(000 $\bar{1}$) acquire large mm. The presence of the surface enhances the spin polarization induced by Co atoms and promotes surface magnetism. Furthermore, even in the absence of magnetic ions, a robust F state is predicted for the O-terminated (0001) ZnO surface.

Our study of the spin resolved electronic structure is based on the *ab-initio* pseudopotential density functional theory within the local spin density approximation. We use the SIESTA package [8] with basis sets formed by multiple-zeta polarized localized numerical atomic or-

bitals (AO). In the case of Zn, we choose double-zeta (DZ) basis for the s and d AOs plus a single-zeta (SZ) p AO. The same type of basis set is used for Co, whereas for O we employ DZ s and p AOs plus a SZ d AO. More details about the conditions of the calculations can be found elsewhere [9].

Since the wurtzite structure is not centrosymmetric, thin layers grown along the crystallographic c -axis may present either the [0001] or the [000 $\bar{1}$] growth direction depending on the substrate orientation. Along this direction, pure hexagonal O and Zn layers alternate, so that the resulting surfaces can be either Zn- or O-terminated, as shown in figure 1. We model them by periodically repeated slabs containing between 15 and 17 ZnO planes, and separated by a vacuum region of at least 15 Å. Bulk-like behaviour is always attained at the innermost central layers. We use a (1×1) two-dimensional (2D) unit-cell to study the undoped bulk and surfaces, and a (2×2) 2D-cell containing four atoms per plane for the Co doped structures. Substitution of one and two Zn atoms by Co gives 3.6 and 7.5% of dopant concentration, respectively. We calculate both symmetric and asymmetric slabs about the central plane. For the former, the two sides of the slab correspond respectively to the inequivalent (0001) and (000 $\bar{1}$) surfaces, which are either both Zn-ended or O-ended; for the second, a Zn and an O surface layer are at opposite ends of the slab. For asymmetric slabs dipolar corrections are applied. The atomic positions are allowed to relax until the forces on the atoms are less than 0.05 eV/Å, and usually below 0.03 eV/Å. Brillouin Zone (BZ) integrations have been performed on a $4 \times 4 \times 1$ Monkhorst-Packard supercell that includes as much as 1800 k-points in the $1/4$ irreducible 2D BZ, although convergence has been verified using $8 \times 8 \times 1$ cells.

The stability of a given surface depends on the partial Oxygen pressure. For a surface in thermodynamic equilibrium, the surface free energy can be obtained from an *ab-initio* total energy calculation in combination with a thermodynamic formalism [10]. In Fig 1 the calculated relative stability of the different defect-free surfaces with

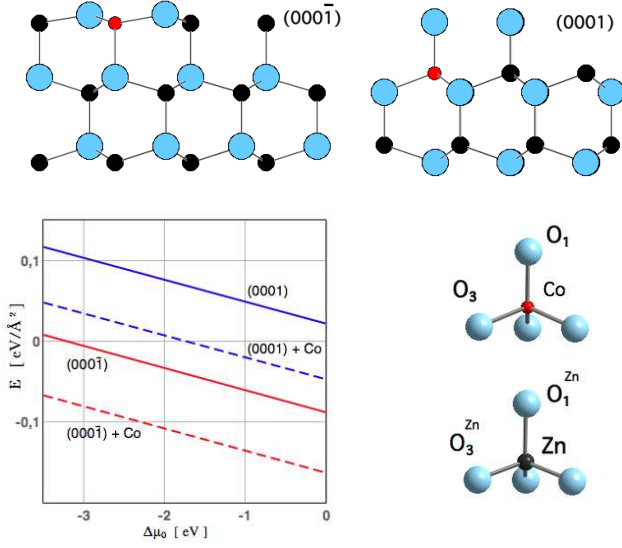


FIG. 1: (color) (Top) Side views of all possible (0001) and (0001) wurtzite ZnO surfaces, indicating the position of substitutional Co at the Co-doped O terminations modelled here. Our labels for the atomic sites are shown in the coordination units at the bottom right side. (Bottom) Relative surface free energy as a function of the O partial pressure for the undoped (solid lines) and Co-doped (dashed) (0001) and (0001) surfaces. For negative energy values the O-termination is more stable than the Zn- one.

[0001] orientation as a function of the Oxygen chemical potential is shown. The O-terminated (0001) surface is found to be stable over the entire admissible range of chemical potentials, in good agreement with experiments [11]. Contrary, for the (0001) surface the most stable surface corresponds to the Zn-termination. However, along the [0001] direction, rough surfaces associated to Zn vacancies and incomplete Oxygen terminations have been observed, and even smooth (0001) O-terminated surfaces are formed under optimum growth conditions [12]. In the following, we will concentrate in the O- surfaces.

First, we analyze the Co-doped O-terminated (0001) surface. For a 3.6% Co concentration, Co substitutes a Zn in the cation subsurface layer (see figure 1). The surface O atoms have an unsaturated dangling bond and are bonded either only to Zn (O₃^{Zn} atoms), or to one Co and two Zn atoms of the subsurface layer (O₃ atoms). The substitution of Zn by Co does not involve a relevant variation of bond distances. However, besides the spin-polarization, Co-doping significantly reduces the surface energy, increasing the surface stability as shown in figure 1. Fig. 2 provides the layer projected density of states (LDOS) of the Co and Co-bonded O atoms at the three uppermost layers, together with that of an inner bulk-like

TABLE I: Magnetic moment (mm, in μ_B) and charge difference with respect to the bulk ($\Delta Q = Q_b - Q$, where Q_b refers to bulk Co or ZnO) of Co and its O neighbours for bulk Co-ZnO, and at the Co and two different O sites of the three outermost layers in the O-ended (0001) and (0001) surfaces, the last either unrelaxed (U) or relaxed (R). The O surfaces for undoped ZnO are also shown. Layers are numbered from the surface (L1) to the bulk.

			O _{L1}	O _{L1} ^{Zn}	Co _{L2}	O _{L3}	O _{L3} ^{Zn}
mm	Co-	Bulk	0.11		2.71	0.12	
		(0001)	0.45	0.03	2.90	0.22	0.03
		(0001) _U	1.39	1.39	2.84	0.20	0.04
		(0001) _R	0.80	1.33	2.05	0.17	0.03
	Und.	(0001)		0.00			0.00
		(0001)		1.40			0.08
ΔQ	Co-	Bulk	-0.03		-0.80	-0.03	
		(0001)	-0.18	-0.06	-0.83	-0.04	0.01
		(0001) _U	-0.58	-0.58	-0.04	0.04	0.02
		(0001) _R	-0.69	-0.57	-0.65	0.09	0.01
	Und.	(0001)		0.11			0.01
		(0001)		-0.58			-0.03

O. For comparison, the corresponding LDOS for bulk Co-ZnO are shown on the left. The calculated mm and Mulliken charges are given in table I. In both, surface and bulk, we find a magnetic ground state which remains insulating. In addition, Co shows a spin-polarized LDOS with a large mm close to $3\mu_B$, the maximum value allowed by Hund's rule. However, there are significant differences when Co is located near the surface or in the bulk. The majority-spin Co 3d states are fully occupied in both cases although the hybridization with the O 2p valence band is stronger for the subsurface Co, which does not show the well defined *e* and *t2* levels seen in bulk Co. Also, while the highest occupied levels in bulk Co are the minority-spin *e* states, both *e* and *t2* minority states are empty in the subsurface Co. Consequently, Co exchange splitting and Co-O hybridization are much larger when Co is close to the surface, leading to a larger induced spin-polarization of the surface Oxygens. In addition, the table suggests certain correlation between mm and charge transfer: surface Oxygen atoms bonded to Co with large mm show a significant decrease of the ionic charge.

There is a gradual evolution of the above described properties for subsurface and bulk Co as the Co distance to the surface increases. Moreover, although Co induced changes are mostly localized around the impurity, their effect extends more at the surface than in the bulk. For example, the mm of the O atoms closer to Co but with no direct bond to it is $0.03\mu_B$ when Co is in the subsurface layer, while it drops to zero when Co is in the bulk, resulting in a total mm per unit cell of 4.76 (3.21) μ_B at the

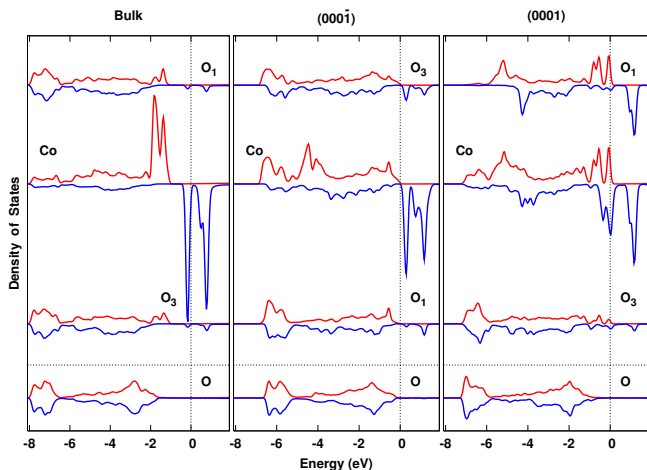


FIG. 2: LDOS for Co and the O atoms bonded to Co at bulk Co-ZnO (left), and at the three uppermost layers of the O-ended (000 $\bar{1}$) (middle) and (0001) (right) surfaces of 3.6% Co-doped ZnO. The top curves refer to the surface plane (L1 in table I), while the bottom ones show the bulk-like LDOS of O at the central layers of each slab. Positive (negative) values correspond to majority (minority) spin states. Energies are referred to E_F .

surface (bulk). This unambiguously demonstrates that the breaking symmetry of the surface promotes magnetism.

We have studied the difference between F and anti-ferromagnetic (AF) ordering substituting an additional Zn by Co at different cation layers (7.5% of Co concentration). The local main features depicted in Fig. 2 are not altered. AF coupling between the Co impurities is favoured whenever Co atoms are separated by more than a ZnO unit, while F coupling becomes stable if there is only an O between them. However, even for an AF alignment of Co atoms, the existence of uncompensated O mm at the surface leads to a net F structure. Nevertheless, the energy difference between states with F and AF Co coupling is always too small, ~ 10 meV, to account for the experimental T_C . Addition of codoping does not modify substantially the magnitude of the coupling, in agreement with previous calculations[13].

Regarding the 3.6% Co-doped (0001) O-ended surface, again the presence of Co atoms close to the surface remarkably increases its stability, in agreement with recent experiments [14], leading to a range of the chemical potential for which the O-termination is the most stable (see figure 1). Oxygen atoms have three unsaturated dangling bonds, and therefore they are onefold coordinated only to the metal atom underneath, either a Co (O_1 atoms) or a Zn (O_1^{Zn} atoms). Due to the low coordination, which is clearly evidenced in the large charge loss, important relaxations occur. For this reason, the unrelaxed and relaxed values are provided in table I. The main effect of relaxation is to modify the Co-O bond distances, which can become as small as 1.5\AA for the O_1 atoms. The short

bond length modifies largely the Co mm. In fact, the Co exchange splitting becomes smaller than that for an impurity in the bulk, as shown in the rightmost panel of figure 2. The Fermi level (E_F) crosses the valence band, leading to a metallic surface. On the other hand, the induced mm of surface Oxygen is almost twice than at the (000 $\bar{1}$) surface, reflecting the stronger hybridization to Co. Nevertheless, the more striking effect is that all the surface Oxygens develop a mm independent of the magnetic character of the cation neighbour, which is even larger for the O_1^{Zn} atoms, $1.3\mu_B$. Further, the LDOS of the two inequivalent surface O (not shown here) show different shapes, pointing to a dissimilar origin of the mm. In summary, it seems like there are two different types of mm for O: one induced by hybridization with the impurity d states, and other which can not be associated to the d electrons.

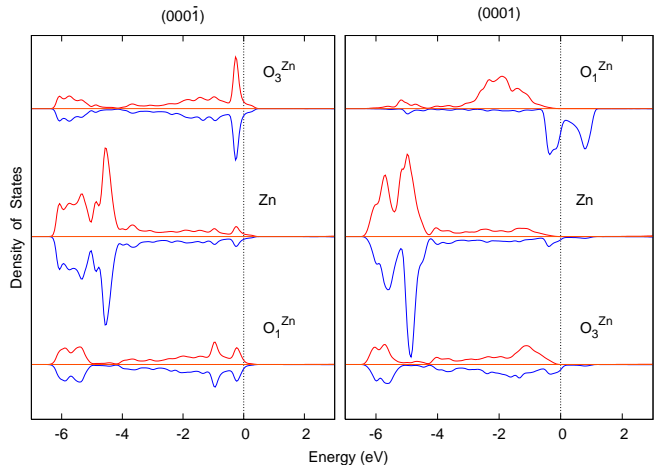


FIG. 3: Same as figure 2 for the three topmost layers of the O-ended undoped ZnO (000 $\bar{1}$) and (0001) surfaces.

To get a further insight on this idea, we have calculated the (000 $\bar{1}$) and (0001) O surfaces of undoped ZnO allowing for the spin degree of freedom. We find that the configuration with ferromagnetically ordered spin moments is favoured at the (0001) surface. The energy reduction due to the spin polarization is 0.6 eV per O, a value in the range of those obtained for magnetic bulk oxides. The LDOS of the undoped surfaces are displayed in figure 3, and the mm and ionic charge differences are also included in table I. Oxygen at the (000 $\bar{1}$) surface presents an occupied large peak close to E_F but it has not an appreciable spin-polarization. On the other hand, a large splitting is observed in the Oxygen atoms at the (0001) surface, which develop a mm very similar to that of O bonded to Zn in the Co-doped surface. Remarkably, the bands crossing E_F correspond to minority-spin levels, leading to a half-metallic system with charge compensating holes of well defined spin polarization. The lower O coordination of the (0001) surface as compared to the (000 $\bar{1}$) one leads

to a lower charge transfer and then to a higher number of $2p$ holes in the O valence band. This different response proves that it is necessary a critical number of $2p$ holes for achieving a magnetic surface. This result corroborates previous findings of correlation between ionic charge and mm on a systematic study of magnetic surfaces of highly ionic oxides[15]. Another peculiarity of Oxygen mm induced by creating $2p$ holes is the highly anisotropic distribution of the magnetic charge, which involves only p -orbitals along specific directions. The crystal field determines where holes are localised: while the majority spin is completely filled and thus adopts the spherical symmetry of the bulk, there is an anisotropic distribution of the minority charge, and holes mainly reside in the p_{xy} orbitals of the (0001) O surface. This is seen in figure 4, which depicts the spin charge density differences (SDD, total charge density minus the superposition of atomic charge densities) for the Co-doped (000 $\bar{1}$) and the undoped (0001) surfaces, evidencing the different orbital contributions to the mm when induced by the $2p$ holes or by Co-O hybridization.

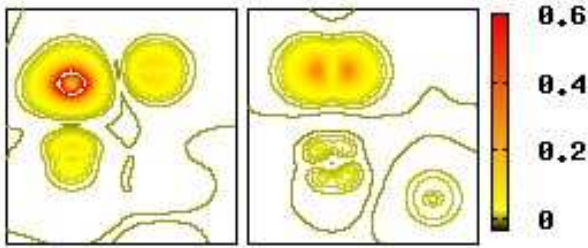


FIG. 4: (color) SDD at the two topmost surface planes of the O-ended (left) Co-ZnO(000 $\bar{1}$) surface around the Co site and (right) undoped ZnO(0001) surface.

In conclusion, the proximity of a surface to a substitutional Co in ZnO enhances the magnetization induced by the magnetic impurity and even for an AF alignment of Co impurities the surface may show uncompensated spins ferromagnetically ordered, although this effect alone does not justify a high T_C . The presence of Co atoms close to the surface remarkably increases its stability. In addition, in the absence of magnetic atoms, p -magnetic states can still develop whenever a critical value of p -holes is exceeded, with a highly anisotropic distribution of the magnetic charge. The existence of oxygen polarised large surface areas can account for some of the spontaneous magnetization reports observed in several ZnO structures, even in the absence of magnetic doping. Also, it can explain why the magnetic state is intimately connected to the actual structure of the sample and the growth conditions. Oxygen p -magnetism associated to uncompensated charge in ionic oxides seems to be a gen-

eral phenomenon which can be related to early reports about the fact that cation-deficient CaO or SrO should be half-metallic ferromagnets [16], the recent proposal of magnetizing oxides by substituting nitrogen for oxygen [17], as well as to the magnetic properties of cation vacancies in II-VI semiconductors [18]. Recently, magnetic states have been reported at the interface between two non-magnetic oxides [19]. This opens new perspectives for the development of the new fascinating field of oxides heterostructures in which the violation of charge compensation may give rise to new magnetic or superconducting states [20].

This research was supported by the Spanish Ministry of Science and Technology under Project MAT2006-05122.

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